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Contaminants of Concern in Dutch Marine Harbor Sediments

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Abstract. The status of the contamination of Dutch marine harbor sediments was reevaluated after a period in which emissions from point sources had been greatly reduced. Data on sediment chemistry from 1999 and 2000 were assessed against screening levels (SLs) selected from available sediment quality guidelines and representing a low probability of adverse biological effects. This yielded a ranking of the environmental hazard of 22 contaminants. Most of the sediments were silty material; every year 15 to 25 million m³ of such material is dredged from Dutch harbors. Some 34% of the volume exceeded one or more SLs. The contaminants of concern were tributyltin (TBT), mineral oil (petroleum hydrocarbons), polychlorinated biphenyls (PCBs), and mercury. The PCB and mercury contamination is the legacy of historic inputs; the TBT and mineral oil contamination is related to present-day shipping activity. Concentrations of trace metals, rare earth elements, organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAHs) were low and apparently of minor environmental concern. It is concluded that the risk assessment would be improved by laboratory testing of adverse biological effects.

Delta areas like that of the Rhine-Meuse have been so intensively used for shipping, agriculture, and for the discharge of urban or industrial effluents that aquatic ecosystems have become seriously contaminated. Fluvial and marine sediments acted as a sink for many of the contaminants that are poorly water-soluble. By the early 1970s, it was recognized that the open-water disposal of such contaminated dredged material seriously threatened the quality of coastal environments in question. This resulted in international guidelines being drawn up for the environmental management of contaminated dredged material (IMO 1998; OSPAR 1998).

In the Netherlands, where coastal harbors are kept accessible to shipping by maintenance dredging, large volumes of dredged material are disposed of offshore. If the dredged material is from

a potentially contaminated location, a permit for disposal is required; one is granted only if the action levels for a suite of contaminants are not exceeded (Ministerie van Verkeer en Waterstaat 1998). Harbor sediments exceeding the action levels must be disposed of in costly confined disposal facilities.

In the last 20 years, emission control measures have significantly reduced inputs to the aquatic environment of the Netherlands. Major reductions in emissions were achieved between 1985 and 1995 at point sources such as petrochemical industries and fertilizer plants. The reductions in aquatic discharges achieved in that period were 60–98% for trace metals, 90% for dioxins, and 80% for organochlorine pesticides (Brongers *et al.* 1998). As a result, the quality of material dredged from the harbors improved significantly (POR 2001) as did the sediments in the Dutch coastal waters (Laane *et al.* 1999). Nowadays, the remaining emissions are predominately from diffuse sources such as treated effluents and runoff from urbanized areas, transportation, and agriculture.

In this paper we will evaluate the present status of the contamination of Dutch marine harbor sediments and will identify the contaminants that are of most environmental concern. This evaluation is part of a larger study on the development of a new chemical–biological framework for assessing contaminated harbor sediments intended for disposal in Dutch coastal waters (Stronkhorst 2003). Chemicals of concern are defined here as those that have the potential to cause adverse biological effects (toxicity), enter the food web (bioaccumulation), and remain in the environment for a long time (persistent). We base our report on a survey conducted in 1999 and 2000 to determine the actual concentrations of trace metals, rare earth elements, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), mineral oil (petroleum hydrocarbons), organochlorine pesticides (OCPs), and organotin. We used published sediment quality guidelines (SQGs) to assess the data.

Materials and Methods

Sediment Sampling

In total, 257 harbor sediment samples and 22 coastal reference sediment samples were collected at sites along the Dutch coast (Figure 1)

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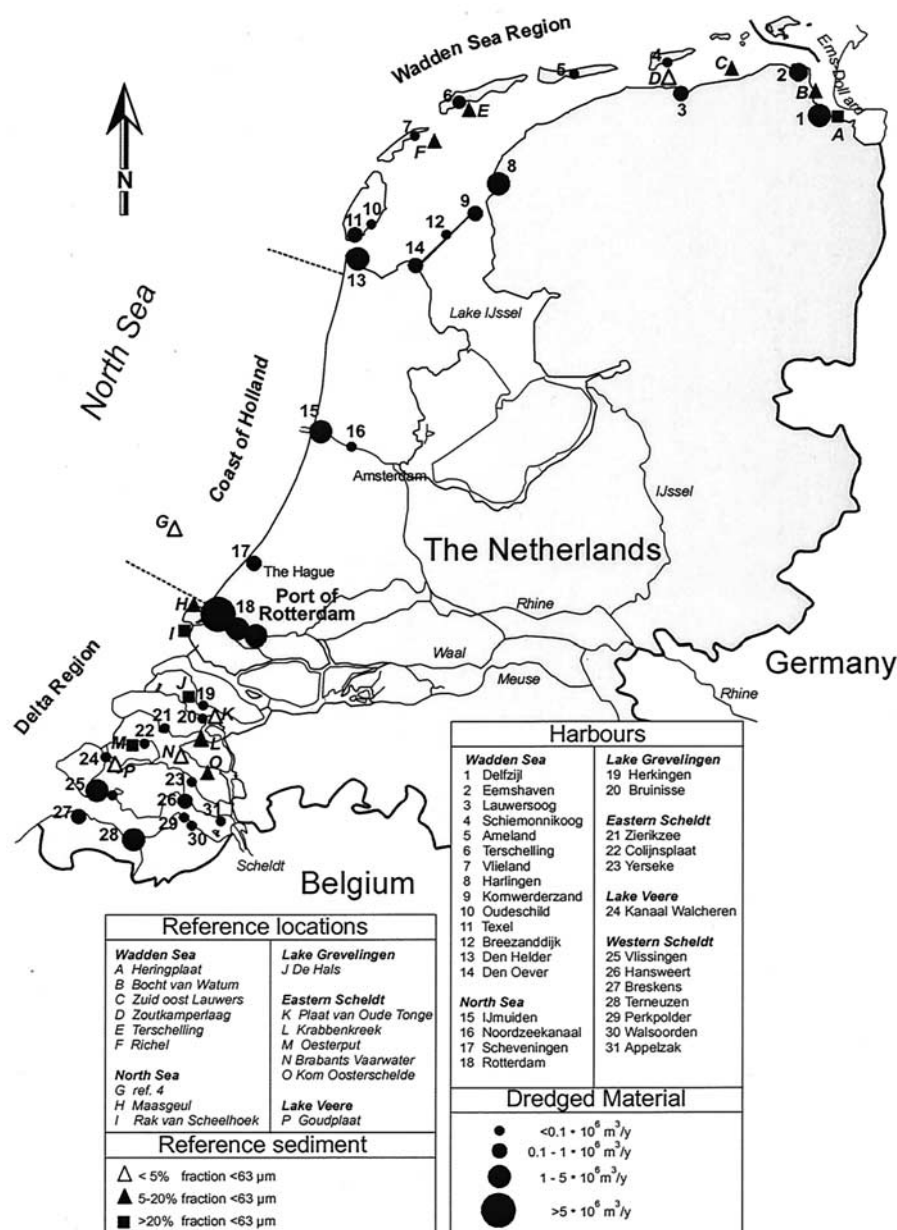


Fig. 1. Harbours and reference locations along the Dutch coast where sediments were sampled during the 1999–2000 survey. Also indicated are the annual volume of dredged material and the sediment texture at the reference sites

in March to August 1999 and April to August 2000. Samples for the analysis of rare earth elements, however, were collected in April 1995 at 45 sites. Composite sediment samples were made following a stratified random sampling strategy. Based on historical data, we divided the harbours into segments of generally homogeneous areas of contamination. In each segment six subsamples were collected with a Van Veen grab (40 cm in width). To obtain the actual status of the most recently deposited sediment, samples were collected from approximately the top 20 cm of the sediment. The samples might, however, represent different time spans due to the differences in sedimentation rates between the harbor sites. After homogenizing the material the samples were stored at 4°C for 1–4 weeks prior to analysis. The reference sediments were selected in different parts of the Dutch coast (Wadden Sea, coast of Holland and Delta region) and with variable fractions of silt and clay. Further, they represent the ambient conditions in Dutch coastal waters in terms of the background anthropogenic influence of present and historic contamination.

Bulk Sediment Characterization

The dry weight fraction was determined at 105°C. Total organic carbon (TOC) content was measured with a carbon analyzer (conversion at 1300°C) according to Dutch standard NEN 5756; grain size distribution (fraction <2, <16, and <63 μm) was measured according to NEN 5753 (a method based on settling velocity). Port authorities and other applicants requiring permits for open water disposal have to provide data on the concentrations in the dredge material of the mandatory list of contaminants, including trace metals, PCBs, PAHs, OCPs, and mineral oil as specified below. Trace metals were determined in microwave acid-digested samples (HNO₃ and HCl mixture in a pressurized system (NEN 5770) with inductive coupled plasma atomic emission spectroscopy (ICP-AES: Cd, Cr, Zn, Cu, Ni, Pb, As; NEN 6426) or cold vapor atomic absorption spectroscopy (CV-AAS; Hg; NEN 5779). OCPs (lindane, hexachlorobenzene [HCB], aldrin,

dieldrin, endrin, telodrin, DDE, DDD, DDT) and PCB (congeners 28, 52, 101, 118, 138, 153, and 180) were quantified in pentane soxhlet extracts after clean-up with a SiO₂ column and determination with gas chromatography with electron capture detection (GC-ECD) according to draft standard NEN 5718. PAHs were quantified with reversed phase HPLC with UV and fluorescence detection in acetone/hexane extracts (according to NEN 5771: naphthalene, acenaphthylene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*] pyrene, benzo[*ghi*]perylene, and benzo[*a*]pyrene. Mineral oil (petroleum hydrocarbons) consisting of the alkanes between C10–40 were extracted from the sediment with acetone/hexane and analyzed with GC with flame ionization detector (FID) according to NEN 5733. In addition to the mandatory parameters, rare earth elements and organotins were analyzed too. The rare earth elements cerium (Ce), lanthanum (La), and neodymium (Nd) were determined with ICP-AES after destruction of the samples according to NEN 6465. The rare earth elements were of interest because of the discharges by, for instance, phosphate processing industries. For the analysis of tributyltin (TBT) and triphenyltin (TPhT), the samples were acidified with hydrochloric acid, extracted with diethylether/tropolone, derivatized by means of a Grignard pentylation reaction, followed by clean-up over deactivated alumina, and analyzed by means of gas chromatography with mass spectrometric detection (GC-MS), slightly modified from the method described by Stäb *et al.* (1996). The analyses were performed by Alcontrol BV, Hoogvliet, The Netherlands. Limits of detection for arsenic, cadmium, chromium, copper, mercury, nickel, lead, and zinc were 4, 0.3, 15, 5, 0.05, 3, 5, and 10 mg/kg dry wt, respectively, for organochlorine pesticides and PCBs congeners 1 µg/kg dry wt, for TBT and TPhT 1 µg Sn/kg, for mineral oil 20 mg/kg, for PAHs compounds 0.01 mg/kg.

Sediment Quality Guidelines (SQGs)

Seven sets of published SQGs were used to evaluate the observed concentrations of contaminants. In the Netherlands, Maximal Tolerable Concentrations (MTC; Crommentuijn *et al.* 2000a, 2000b) are used to assess the general quality of sediments in open waters. MTCs are based on the log-logistic distribution of NOECs and are assumed to be protective for 95% of the aquatic species. Under the Water Pollution Act, when MTCs are exceeded, additional source control measures are mandatory. The Dutch Intervention Value (IV; CIW 2000) represents hazardous concentrations for organisms (or humans) and when exceeded, additional investigations for sediment clean-up at that site are mandatory. Both these SQGs are based on the sediment-water equilibrium partitioning theory (EqP; Di Toro *et al.* 1991) and are expressed for a standard sediment with 5.8% OC and 25% clay.

Two empirically derived guidelines were used: the effect-range-low (ERL) and effect-range-median (ERM) for 18 compounds as proposed by Long *et al.* (1995). The ERL and ERM represent the concentrations below which adverse effects are expected to occur rarely and frequently, respectively. They were established by using simultaneous observation of sediment contamination and sediment toxicity or benthic impacts reported for estuaries and marine bays throughout North America. The ERL and ERM are equal to the tenth and fiftieth percentile concentration of each contaminant represented in the effect data set, respectively. Consequently, they are based on covariance rather than causality. Further, the ERL and ERM do not consider differences in the physicochemical properties of the sediment. As a combined measure of sediment contamination, we used the mean ERM quotient (m-ERM-Q), calculated according to (Long *et al.* 1998):

$$\text{m-ERM-Q} = \sum (C_i/\text{ERM}_i)/n \quad (1)$$

where C_i = bulk sediment concentration of compound i , ERM_i = ERM for compound i , n = number of compounds.

Several jurisdictions have set pragmatic guidelines for dredged material intended for open water disposal. We considered (i) the Dutch Uniform Content Test (UCT) which is a set of absolute pass/fail criteria for disposal into coastal waters of the North Sea (CIW 2000) and (ii) dredged material screening levels (SL) and maximum levels (ML) for open-water disposal in the State of Washington, USA (PSSDA 2000). Dredged material with levels of contaminants below PSSDA-SLs is acceptable for ocean disposal, but when these levels are exceeded, the material requires further biological testing with bioassays. When concentrations of contaminants are very high and exceed the PSSDA-MLs, it is very likely that biological testing will identify adverse effects.

The MTC, UCT, and IV are defined for the standard sediment mentioned above; no normalization is applied to ERL, ERM, and PSSDA values.

Screening Levels

To determine the chemicals of concern in the Dutch harbor sediments, we selected screening levels (SLs) for each contaminant. Intended to represent concentrations that have a low probability of causing adverse biological effects, these SLs were set at the lowest value out of the MTC, PSSDA-SL, and ERM values. In addition to the SQGs mentioned, we considered other published guideline values or spiked sediment toxicity test results for several contaminants that seemed most critical. The extent to which SLs were exceeded was determined by calculating the ratio between the observed concentration and accompanying SL.

Data Analysis

Concentrations below detection limit (DL) were processed as observations at half the DL (Clarke 1998). Principal components analysis (PCA) was performed using custom routines in MATLAB (Moler 1998) to obtain a decomposition of the data into two relevant principal components, as judged by an Eigenvalue >1. Correlations between (log transformed) contaminants and between physicochemical characteristics were determined for those variables with more than 80% of the observations above DL. Records on the annual volumes of dredged sediments per harbor section were used to quantify the consequences of using the different SQGs.

Reference sediments were categorized into coarse (less than 20% fine particles <63 µm) and fine sediments (more than 20% fine particles <63 µm). The latter group is comparable to silty harbor sediments.

Results

Volumes and Physicochemical Characterization

Every year, 15 to 25 million m³ is dredged from the 31 harbors investigated (Figure 1). Large amounts are dredged from the port of Rotterdam (18) and from the harbors of Delzijl (1), Harlingen (8), Den Helder (13), and Ymuiden (15).

The harbor sediments varied strongly in their physicochemical properties (Table 1). Most samples, however, were silty sludges with a small dry weight fraction (median of 40%), large fraction of fine sediment <63 µm (median of 50%), and

Table 1. Physicochemical variables of harbor sediments and reference sediments along the Dutch coast, 1999–2000

| | | Grain size fraction* | | | |
|--|------------|----------------------|-----------|-----------|----------|
| | Dry wt (%) | % < 2 μm | % < 16 μm | % < 63 μm | TOC* (%) |
| Harbor sediment ^a | | | | | |
| Minimum | 11 | <1 | <1 | <1 | <0.5 |
| 5th perc. | 24 | 4 | 7 | 11 | 1.0 |
| Median | 40 | 22 | 36 | 50 | 3.3 |
| 95th perc. | 70 | 33 | 53 | 70 | 5.5 |
| Maximum | 87 | 38 | 60 | 74 | 9.8 |
| Coarse reference sediment ^b | | | | | |
| Minimum | 62 | <1 | <1 | 1 | 0.3 |
| 5th perc. | 62 | <1 | <1 | 1 | 0.3 |
| Median | 74 | 1 | 2 | 8 | 0.3 |
| 95th perc. | 81 | 5 | 8 | 19 | 1.6 |
| Maximum | 85 | 6 | 10 | 19 | 2.1 |
| Fine reference sediment ^c | | | | | |
| Minimum | 36 | 5 | 7 | 20 | 0.9 |
| 5th perc. | 41 | 5 | 7 | 20 | 1.0 |
| Median | 55 | 8 | 13 | 26 | 2.4 |
| 95th perc. | 63 | 20 | 32 | 66 | 5.3 |
| Maximum | 65 | 23 | 36 | 76 | 5.5 |

* Grain size fractions and total organic carbon (TOC) are expressed as percentage of dry weight.

^a $n = 257$; ^b grain size fraction < 63 μm of less than 20%, $n = 15$; ^c grain size fraction < 63 μm of 20% or more, $n = 7$.

intermediate amount of organic carbon (median 3.3% TOC). Of the 22 reference sediments, 15 were coarse and seven were fine-grained. The silty reference sediments had fractions of fine particles that were half to one-third the median values for harbor sediments (Table 1).

PCA analysis of the physicochemical characteristics yielded a decomposition with only a single relevant component, indicating that all five physical characteristics (grain size <2, <16, and <63 μm , fractions dry weight and organic carbon) that were investigated are highly collinear. Figure 2A shows the loadings (i.e. the influence of the original variables on the components) of the physicochemical characteristics on the first two principal components. PC1 represents 87% of the variance in the dataset, whereas PC2 covers only 7%. The three grain size fractions were almost indistinguishable. The sediment dry weight was inversely proportional to the amount of silt. Organic carbon was the only characteristic loading on the second principal component, indicating that there is some variability in organic carbon content that is not related to the amount of silt.

Observed Concentrations of Contaminants

Basic statistics on the levels of organic compounds in the harbor sediments indicate the levels of PAHs, mineral oil, PCBs, and TBT vary by two to three orders of magnitude (Table 2). Several reference sediments also had appreciable median levels of these constituents but at half or one-tenth of the levels in harbors. Harbor sediments from the center of the port of Rotterdam ($n = 50$) had the highest geometric mean concentrations of PAHs (3 mg/kg or 93 mg/kg OC), mineral oil (536 mg/kg), and PCBs (52 $\mu\text{g/kg}$) and the harbor of Harlingen had the highest geometric mean TBT concentration (85 $\mu\text{g Sn/kg}$). In most of the sediments investigated, concentrations of TPhT, DDT, and HCB were low or—in the case of aldrin,

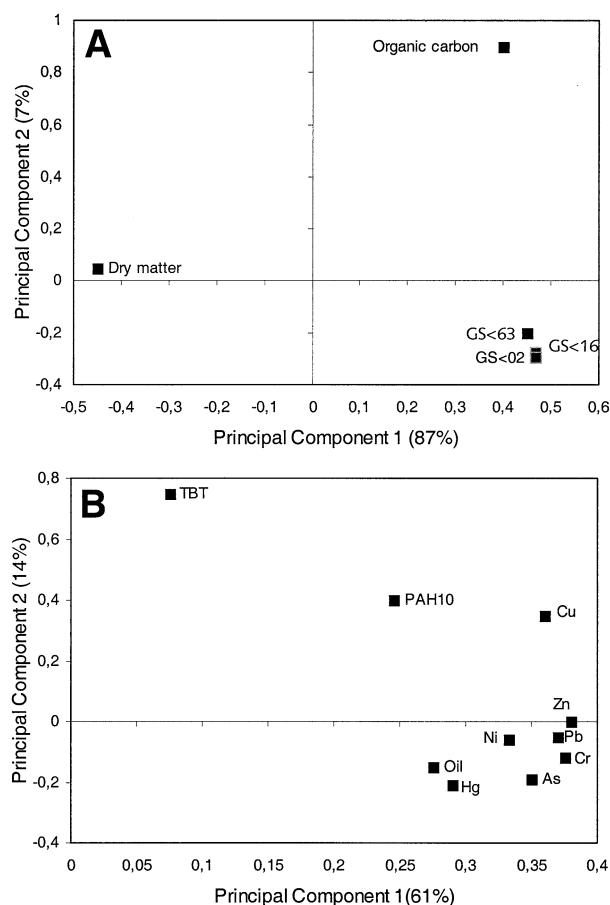


Fig. 2. Loading plot of the first two principal components for (A) physicochemical parameters and (B) all contaminants with more than 80% of the observations above level-of-detection. GS = grain size fractions (μm)

Table 2. Organic contaminants in harbor sediments and reference sediments along the Dutch coast, 1999–2000

| | $\Sigma 13$ -PAH | Oil | $\Sigma 7$ -PCB | Σ -Drins ^d | TBT | TPhT | Lindane | Σ -DDT | HCB |
|--|------------------|------|-----------------|------------------------------|------|------|---------|---------------|-----|
| Harbor sediment ^a | | | | | | | | | |
| Minimum | <0.1 | <20 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 5th perc. | <0.1 | <20 | <1 | <1 | 2 | <1 | <1 | <1 | <1 |
| Median | 1.4 | 140 | 10 | <1 | 23 | <1 | <1 | <1 | <1 |
| 95th perc. | 6.4 | 1100 | 76 | <1 | 250 | 5 | <1 | 2 | 4 |
| Maximum | 36 | 3600 | 456 | 2635 | 2700 | 44 | 3 | 40 | 67 |
| Coarse reference sediment ^b | | | | | | | | | |
| Minimum | <0.1 | <10 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 5th perc. | <0.1 | <10 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Median | <0.1 | <10 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 95th perc. | 0.5 | 51 | 8 | <1 | 21 | <1 | <1 | <1 | 10 |
| Maximum | 0.5 | 80 | 21 | <1 | 36 | <1 | <1 | <1 | 17 |
| Fine reference sediment ^c | | | | | | | | | |
| Minimum | <0.1 | 10 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 5th perc. | <0.1 | 10 | <1 | <1 | 1 | 1 | <1 | <1 | <1 |
| Median | 0.7 | 50 | 4 | <1 | 2 | 1 | <1 | <1 | <1 |
| 95th perc. | 1 | 137 | 13 | <1 | 3 | 1 | <1 | <1 | <1 |
| Maximum | 1 | 140 | 15 | <1 | 3 | 1 | <1 | <1 | <1 |

Concentrations of PAH are expressed in mg/kg OC, of mineral oil in mg/kg dry wt, TBT and TPhT in $\mu\text{g Sn/kg}$, and the other compounds in $\mu\text{g/kg}$ dry wt.

^a $n = 257$; ^b grain size fraction < 63 μm of less than 20%, $n = 15$; ^c grain size fraction < 63 μm of 20% or more, $n = 7$; ^d Aldrin, Dieldrin, and/or Endrin.

dieldrin, endrin, telodrin, and lindane—were undetectable. Levels of drins (aldrin, dieldrin, endrin, telodrin) and HCB were very high in two sediments from the central part of the port of Rotterdam and the level of Σ -DDT in sediment from harbor 14 was exceptionally high.

Concentrations of metals and rare earth elements varied by one order of magnitude (Table 3). Levels of trace metals that were a half or one-third lower were observed in fine reference sediments. Sediments from the center of the port of Rotterdam had the highest geometric mean levels of cadmium (2.1 mg/kg), mercury (0.8 mg/kg), copper (51 mg/kg), and zinc (303 mg/kg).

Of the sediments investigated, 42% had a mean ERM Quotient (m-ERM-Q) below 0.1, 55% had m-ERM-Qs between 0.1 and 0.5, and 3% had an m-ERM-Q above 0.5.

Seventy-five percent of the variance in the chemical data set is described by the first two principal components of the PCA; the loading vectors are shown in Figure 2B. The metals zinc, nickel, lead, arsenic, and chromium were closely related, while mercury was more related to mineral oil. TBT determines most of the variability in the second principal component. The levels of copper and PAH lie in between those for other metals and TBT.

Comparison with Sediment Quality Guidelines

Table 4 shows the SQGs selected in this study to assess the harbor sediments. There were major differences in the estimated volume of dredged material that fails the various sets of SQGs (Figure 3). Less than 0.5% of the volume of dredged material failed the PSSDA-Maximum Level and Dutch Intervention Value, but the whole volume failed the MTC because all sediments failed the stringent criterion for TBT (0.7 $\mu\text{g Sn/kg}$, which is below DL). Approximately 90% of the volume failed the ERL, largely because the criteria for mercury and

arsenic were exceeded. Arsenic, however, is not regarded as a chemical of concern because the ERL for arsenic was below its natural background level of 15 mg/kg for North Sea sediments (Laane *et al.* 1992). The comparison with the PSSDA Screening Level suggests that 25% of the material needs additional biological testing. According to the PSSDA-SLs, the most critical variables were mercury and PCBs. According to the national Uniform Content Test (UCT) some 7% of the sediment by volume could not be permitted to be disposed of offshore; the most critical variables were copper and phenanthrene.

To identify chemicals of concern in the Dutch harbor sediments we selected a screening level (SL) for 22 contaminants or contaminant groups (Table 4). The consensus-based guideline value of 40 $\mu\text{g/kg}$ dry wt proposed by MacDonald *et al.* (2000) was used as screening level for $\Sigma 7$ -PCBs in the Dutch harbor sediments. This guideline has been set for total PCBs based on analysis of PCB mixtures; it is derived from data on estuarine and coastal sediments from North America with an organic carbon content of approximately 1% (MacDonald *et al.* 2000). We chose this consensus-based value as the SL for $\Sigma 7$ -PCBs, assuming that the portion of $\Sigma 7$ -PCBs within total PCBs roughly counterbalances the higher fraction of organic carbon in the Dutch harbor sediments compared to North American sediments mentioned above. For the OCPs and trace metals the lowest value of three set guidelines (MTC, ERM, and PSSDA-SL) was used as screening level. For PAHs, our preference was for the consensus-based guideline value for $\Sigma 13$ -PAH of 290 mg/kg OC proposed by Swartz (1999). We converted this value to the median organic carbon content of the harbor sediment (3.3%), resulting in a SL of 10 mg/kg dry wt. For mineral oil, a MTC of 1000 mg C10–40/kg has been reported but it has no ecotoxicological basis (CIW 2000). As an alternative for deriving a screening level for mineral oil we

Table 3. Arsenic, trace metals, and rare earth elements in harbor sediments and reference sediments, along the Dutch coast, 1999–2000

| | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn | Ce | La | Nd |
|--|----|------|-----|-----|-------|----|-----|------|----------------|----|----|
| Harbor sediment ^a | | | | | | | | | | | |
| Minimum | <4 | <0.3 | <15 | <5 | <0.05 | <3 | <5 | <10 | 8 | 3 | 3 |
| 5th perc. | 6 | <0.3 | 16 | 6 | 0.1 | 6 | 7 | 45 | 16 | 5 | 7 |
| Median | 14 | 0.5 | 44 | 22 | 0.3 | 18 | 41 | 150 | 30 | 9 | 16 |
| 95th perc. | 21 | 3.0 | 84 | 94 | 1.1 | 35 | 94 | 411 | 74 | 37 | 32 |
| Maximum | 69 | 8.4 | 200 | 180 | 9.9 | 80 | 250 | 1000 | 183 | 94 | 83 |
| Coarse reference sediment ^b | | | | | | | | | | | |
| Minimum | 2 | 0.2 | 8 | 3 | 0.0 | 2 | 3 | 5 | - ^d | - | - |
| 5th perc. | 2 | 0.2 | 8 | 3 | 0.0 | 2 | 3 | 6 | - | - | - |
| Median | 3 | 0.2 | 8 | 3 | 0.0 | 4 | 3 | 19 | - | - | - |
| 95th perc. | 7 | 0.2 | 16 | 12 | 0.1 | 6 | 9 | 48 | - | - | - |
| Maximum | 8 | 0.2 | 18 | 19 | 0.1 | 6 | 13 | 49 | - | - | - |
| Fine reference sediment ^c | | | | | | | | | | | |
| Minimum | 5 | 0.2 | 18 | 5 | 0.0 | 7 | 3 | 34 | - | - | - |
| 5th perc. | 6 | 0.2 | 19 | 5 | 0.0 | 7 | 6 | 38 | - | - | - |
| Median | 8 | 0.5 | 23 | 10 | 0.1 | 10 | 23 | 83 | - | - | - |
| 95th perc. | 14 | 0.8 | 43 | 24 | 0.4 | 19 | 44 | 173 | - | - | - |
| Maximum | 16 | 0.9 | 48 | 28 | 0.5 | 20 | 51 | 200 | - | - | - |

Concentrations are in mg/kg dry wt.

^a $n = 257$ or 45 in case of Ce, La, and Nd; ^b grain size fraction < 63 μm of less than 20%, $n = 15$; ^c grain size fraction < 63 μm of 20% or more, $n = 7$; ^d no data.

used toxicity data from recent experiments by Brils *et al.* (2002) with the ten-day amphipod *Corophium volutator* test and 14-day heart urchin *Echinocardium cordatum* test using silty marine sediments freshly spiked with DMA gasoil and HV46 hydraulic oil. The NOECs for DMA, the oil mainly consisting of the C10-19 alkane fraction, were 40–87 mg/kg. HV46, a heavier oil containing C20-39 alkanes in particular, was less toxic and had NOECs of 734 to 2708 mg/kg. Indicative data from our study indicated that C10-19 accounted for 15–45% of the total petroleum hydrocarbons C10-40 (data not shown). Assuming an average NOEC for DMA of 60 mg/kg and an average C10-19/C10-40 ratio of 0.3, we set the SL at 200 mg C10-40/kg. For TBT we could not use the reported guidelines to assess our bulk sediment data because they had been set for interstitial water (PSSDA) or below the detection level (MTC). Instead, we used no-observed-effect concentrations (NOECs) from experiments with TBT spiked sediments conducted by Meador and Rice (2001) and Meador *et al.* (2002). Chronic exposure of the marine polychaete *Armandia brevis* and estimates for prey species of salmonid fish to these sediments resulted in NOECs for sublethal effects of respectively 35 μg TBT⁺/kg dry sediment with 0.6% OC and 6000 μg TBT⁺/kg OC. These values were converted to the median organic carbon content in the Dutch harbor sediments of 3.3% TOC and expressed on a tin basis (Sn) by using the ratio TBT⁺/Sn of 2.44. This resulted in NOECs of 80 and 81 μg Sn/kg, respectively. Consequently, the SL was set at 80 μg Sn/kg dry wt.

Chemicals of Concern

The SLs for mineral oil, TBT, PCBs, and mercury were exceeded in 14–35% of the harbor sediments (Figure 4). In most harbors, mineral oil, TBT, and mercury contamination is of

concern, while PCBs are a potential problem in sediments from the central section of the port of Rotterdam (Table 5). The SLs of other metals (Cd, Cu, Ni, Pb, Zn), drins (dieldrin, endrin, aldrin), HCB, DDT, and PAHs were rarely exceeded (1–6% of the cases) and all samples met the screening levels for chromium, rare earth elements (Nd, La, Ce), lindane, and TPhT (Figure 4). Harbor sediments with less than 10% clay and silt (<63 μm), as well as all reference sediments had levels below SLs. Overall, 34% of the volume of material dredged from the Dutch harbors failed the selected SLs.

Figure 5 shows the geographical distribution of the contamination for the most contaminated harbor area, that is, the central part of the port of Rotterdam (Figure 5). Except for two sites, mineral oil, PCBs, and metals (in particular mercury) exceeded the SLs throughout the area by a factor of 2–44. More locally, SLs for TBT, drins, and PAHs were exceeded.

Discussion

This study identified mineral oil, TBT, PCBs, and mercury as the most important chemicals of concern. These compounds are persistent in silty anaerobic marine sediments and can cause toxic effects in marine life (Daan *et al.* 1992; Ten Hallers *et al.* 1994; Brouwer *et al.* 1989; Wolfe *et al.* 1998). Bioaccumulation is a particular phenomenon for PCBs and mercury. Under US regulations for open water disposal of dredged material, an in-depth assessment of bioaccumulation is required when the estimated Theoretical Bioaccumulation Potential exceeds a critical body residue (US-EPA/US-ACE 1998) or when bioaccumulation trigger values for sediments are exceeded (PSDDA 2000). The SLs for PCBs and mercury we selected were well below both these indicators and therefore these SLs are regarded as being protective for the phenomena of bioaccumulation. Both the PCBs and mercury in our samples reflect

Table 4. Selected sediment quality guidelines for marine sediments

| | MTC ^a | IV ^b | ERL ^c | ERM ^d | PSSDA-SL ^e | PSSDA-ML ^f | UCT ^g | Additional values |
|-------------------------------------|------------------|-----------------|------------------|------------------|-----------------------|-----------------------|------------------|-------------------|
| PCBs and OCPs (µg/kg dry wt) | | | | | | | | |
| Σ ₇ -PCB | - | 1000 | 22.7 | 180 | 130 | 775 | - | 40 ^h |
| Indiv. PCB congeners ⁱ | <u>4</u> | - | - | - | - | - | 30 | - |
| Aldrin | <u>6</u> | - | - | - | 10 | - | 30 | - |
| Dieldrin | 450 | 4000 | 0.02 | <u>8</u> | 10 | - | 30 | 924 ^j |
| Endrin | <u>4</u> | - | - | - | - | - | 30 | 33 ^k |
| Lindane | 230 | - | - | - | <u>10</u> | - | 20 | - |
| Σ-DDT | 12 | 4000 | 1.58 | 46.1 | <u>6.9</u> | 69 | 20 | - |
| Hexachlorobenzene | <u>5</u> | - | - | - | 22 | 230 | 20 | - |
| Metals and REE (mg/kg dry wt) | | | | | | | | |
| Arsenic | <u>55</u> | 55 | 8.2 | 70 | 57 | 700 | 29 | - |
| Cadmium | 12 | 12 | 1.2 | 9.6 | <u>5.1</u> | 14 | 4 | - |
| Chromium | <u>380</u> | 380 | 81 | 370 | - | - | 120 | - |
| Copper | <u>73</u> | 190 | 34 | 270 | 390 | 1300 | 60 | - |
| Mercury | 10 | 10 | 0.15 | 0.71 | <u>0.41</u> | 2.3 | 1.2 | - |
| Nickel | <u>44</u> | 210 | 20.9 | 51.6 | 140 | 370 | 45 | - |
| Lead | 530 | 530 | 46.7 | <u>218</u> | 450 | 1200 | 110 | - |
| Zinc | 620 | 720 | 150 | 410 | <u>410</u> | - | 365 | - |
| Cerium | <u>220</u> | - | - | - | - | - | - | - |
| Lanthanum | <u>510</u> | - | - | - | - | - | - | - |
| Neodymium | <u>480</u> | - | - | - | - | - | - | - |
| PAHs and Mineral Oil (mg/kg dry wt) | | | | | | | | |
| Anthracene | 0.1 | - | 0.0853 | - | 0.96 | 13 | 0.8 | - |
| Benzo[a]anthracene | 0.4 | - | 0.261 | 1.6 | 1.3 | 5.1 | 0.8 | - |
| Benzo[a]pyrene | 3 | - | 0.43 | 1.6 | 1.6 | 3.6 | 0.8 | - |
| Benzo[ghi]perylene | 8 | - | - | - | 0.67 | 3.2 | 0.8 | - |
| Chrysene | 11 | - | - | 2.8 | 1.4 | 21 | 0.8 | - |
| Phenanthrene | 0.5 | - | 0.016 | 1.5 | 1.5 | 21 | 0.8 | - |
| Fluoranthene | 3 | - | 0.665 | 5.1 | 1.7 | 30 | 2 | - |
| Indeno[1,2,3cd]pyrene | 6 | - | 0.6 | - | 0.6 | 4.4 | 0.8 | - |
| Naphthalene | 0.1 | - | 0.16 | 2.1 | 2.1 | 2.4 | 0.8 | - |
| Σ ₁₃ -PAH | - | - | - | - | - | - | - | 10 ^l |
| Mineral oil | 1000 | 5000 | - | - | - | - | 1250 | 200 ^m |
| Organotin (µg Sn/kg dr wt) | | | | | | | | |
| TBT | 0.7 | 2500 | - | - | - | - | - | 80 ⁿ |
| TPhT | 0.8 | - | - | - | - ^o | - ^o | - | (80) ^p |

Underlined values are used in this paper as screening levels (SLs) to assess the Dutch harbor sediments.

^a Maximal permissible concentration; ^b intervention value; ^c effect range low; ^d effect range median; ^e Puget Sound dredged disposal assessment screening level; ^f PSSDA maximum level; ^g (Dutch) uniform content test; ^h based on MacDonald *et al.* (2000); ⁱ IUPAC congeners 28, 53, 101, 118, 138, 153, 180; ^j US EPA (2000a); ^k US EPA (2000b); ^l based on Swartz (1999); ^m based on Brils *et al.* (2002); ⁿ based on Meador and Rice (2001), Meador *et al.* (2002); ^o 0.15 µg/L interstitial water; ^p SL for TBT used as a surrogate.

historic inputs; the emissions of these contaminants to Dutch surface waters have virtually ceased (Brongers *et al.* 1998). The contamination with TBT and mineral oil, however, are the result of present-day shipping: small oil spills and the leaching of TBT from the antifouling paints on ship hulls. Figure 2B illustrated that the distribution of TBT in harbors is quite different from that of other contaminants. This could be due to the fact that TBT originates from marine vessels, while the other compounds mainly come from land-based sources. Recent information on the state-of-the-art of organotin analysis indicates that the reliable analysis of organotin compounds is complex (Ariese *et al.* 1999; Smedes *et al.* 2000), and that accuracy and precision of currently available methods for TBT are less favorable in comparison to the more robust methods for traditional compounds (e.g. PCBs, PAHs, OCPs, trace metals). Although the TBT methods applied in this study were not subjected to the severe quality control conditions recom-

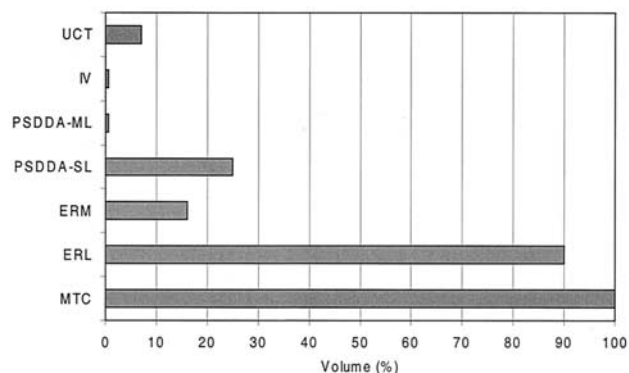


Fig. 3. Relative volume of dredged material that fail different sediment quality guidelines

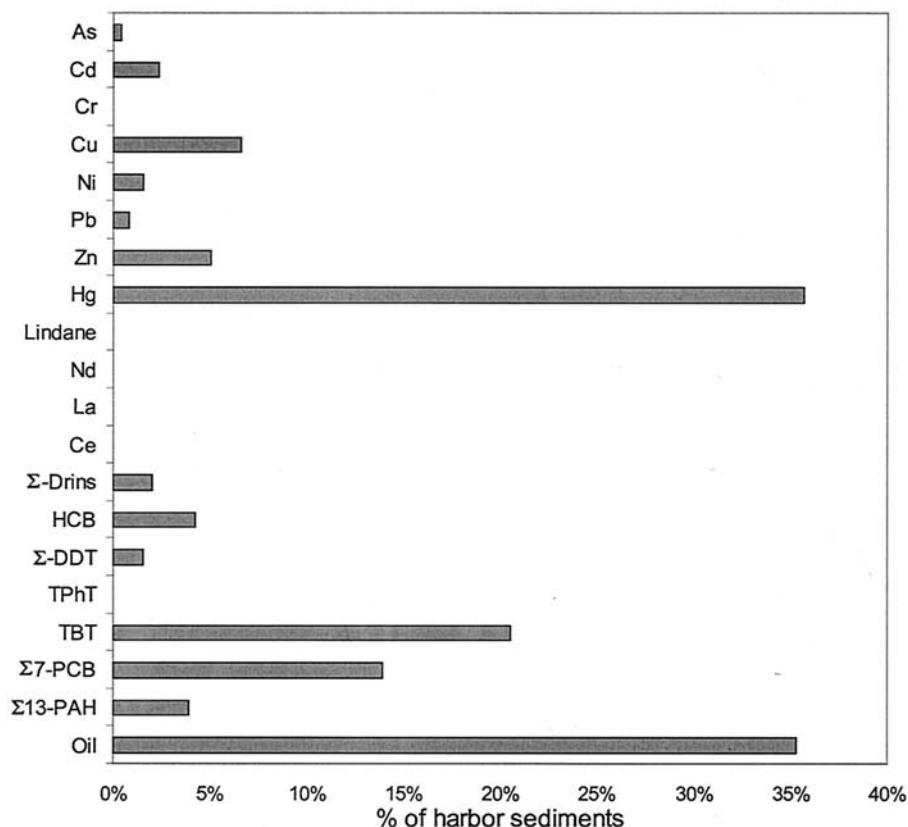


Fig. 4. Percentage of investigated sediments from harbors along the coast of the Netherlands that exceed the screening levels for a suite of contaminants

Table 5. Percentage of sediments from harbors along the Dutch coast that exceed the proposed screening levels^a

| Harbor No. (n) | Oil | Σ ₁₃ -PAH | Σ ₇ -PCB | TBT | Drins | HCB | Cu | Hg | Zn |
|--------------------|-----------|----------------------|---------------------|-----------|----------|----------|----------|-----------|----------|
| 1 (14) | 7 | 0 | 0 | 36 | 0 | 21 | 0 | 64 | 0 |
| 2 (6) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 (5) | 20 | 0 | 0 | 60 | 0 | 0 | 0 | 0 | 0 |
| 8 (18) | 39 | 6 | 0 | 44 | 0 | 0 | 6 | 22 | 6 |
| 4,5,6,7,10,11 (12) | 8 | 0 | 0 | 42 | 0 | 0 | 8 | 8 | 0 |
| 9,12,14 (12) | 0 | 0 | 0 | 8 | 0 | 8 | 0 | 25 | 0 |
| 13 (12) | 33 | 8 | 8 | 42 | 0 | 0 | 8 | 25 | 8 |
| 15 (33) | 27 | 6 | 0 | 15 | 0 | 0 | 0 | 27 | 0 |
| 16 (4) | 25 | 25 | 0 | 25 | 0 | 0 | 25 | 50 | 0 |
| 17 (8) | 25 | 0 | 0 | 38 | 0 | 0 | 13 | 88 | 13 |
| 18—west (20) | 5 | 0 | 0 | 5 | 0 | 0 | 0 | 5 | 0 |
| 18—middle (22) | 50 | 0 | 5 | 18 | 0 | 0 | 0 | 27 | 0 |
| 18—central (50) | 88 | 6 | 66 | 16 | 16 | 14 | 22 | 84 | 20 |
| 19,20 (4) | 0 | 0 | 25 | 25 | 0 | 0 | 0 | 0 | 0 |
| 21,22,23 (6) | 17 | 17 | 0 | 33 | 0 | 0 | 0 | 0 | 0 |
| 25 (10) | 20 | 0 | 0 | 10 | 0 | 0 | 0 | 0 | 0 |
| 27 (3) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 28 (8) | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 0 |
| 26,29,30,31 (7) | 43 | 0 | 0 | 0 | 0 | 0 | 0 | 29 | 0 |
| All (257) | 35 | 4 | 14 | 21 | 3 | 4 | 6 | 35 | 5 |

None of the SLs were exceeded in reference sediments.

^a Excluding compounds with a low frequency (<2%) of exceeding the SL.

mended by Smedes *et al.* (2000), estimated ranges for precision (up to 45%) and accuracy (40–160%) of the methods applied in this study (unpublished results from a national audit: A. S. de Jong, RIKZ, personal communication) do not affect the con-

clusions drawn in the previous section. Since 1991, several European countries have banned the use of TBT on small ships (<25 m); its worldwide application on larger, sea-going vessels is expected to cease within the next five years (IMO 2001).

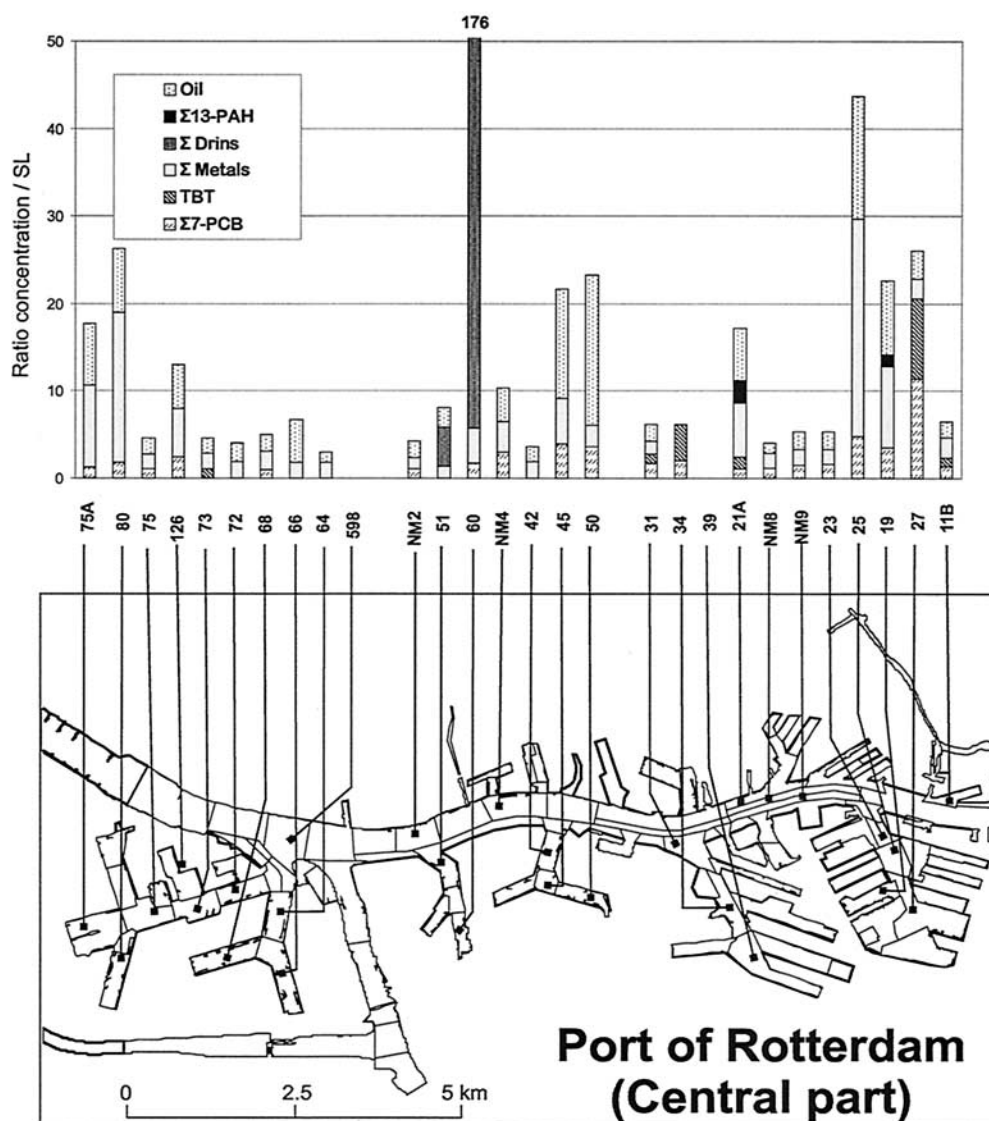


Fig. 5. Extent by which the screening levels (SLs) were exceeded in the central part of the port of Rotterdam. Contaminants that met the SLs were omitted

Nevertheless, it is likely that during the next decade managers of dredged material will be confronted with TBT as a contaminant of concern, because it has a long half-life of many years in anaerobic silty sediments (Mora *et al.* 1995).

As neither mineral oil nor TBT are on the ERL and ERM list of compounds, it is questionable whether the predicted 42% of Dutch harbor sediments with mean ERM Quotients below 0.1 do indeed have a low probability of causing adverse biological effects. North American sediments with m-ERMs below 0.1, however, have shown an acceptable low frequency of mortality in the amphipod tests with *Rhepoxynius abronius* and *Ampelisca abdita* (Long *et al.* 1998, 2000).

In our study the SLs for rare earth elements, TPhT, chromium, and lindane were never exceeded, from which we conclude that routine analysis of these compounds in dredged material is unnecessary. The same might apply to cadmium, nickel, lead, Σ-DDT, aldrin, dieldrin, and endrin, which rarely exceeded the SLs (<2%).

In contrast to other national SQGs in the Netherlands (i.e.,

MTC, IV, and UTC) that require normalization and are expressed in terms of a standard sediment, the SL values in our study are expressed on a dry weight basis, without a correction for the content of the fractions organic carbon or clay. When *in situ* sediment is being assessed, normalization can improve the estimation of ecological risks, but this is not actually necessary when disposing of dredged material. The dredged material is dumped on the seabed under nonequilibrium conditions, as the silts and associated contaminants are redistributed and mixed with other sediments (Spanhoff and de Kok 1990; Macmanus and Prandle 1997). Furthermore, to effectively combat marine pollution from the disposal of dredged material, confined disposal, or sediment treatment facilities must be exploited optimally, i.e. by giving priority to dredged materials with the highest absolute pollutant concentrations, rather than the highest normalized values. We therefore conclude that pass/fail criteria for dredged material should not be based on normalized concentrations in the harbor sediments, as far as decisions on open-water disposal in a high-energy environment is concerned.

The UCT values for metals, PCBs, PAHs, and OCPs were set pragmatically during the early 1990s, with dredged material management in the Netherlands in mind. A comparison with the MTC and PSSDA-Screening Levels suggests that most of these pass/fail criteria appear to be protective for the marine environment. However, we consider the UCT criteria for PCB (30 $\mu\text{g/kg}$ for individual congeners), for mineral oil (1250 mg/kg), and the omission of a TBT criterion to be too liberal, given the consensus-based guideline for PCBs (McDonald *et al.* 2000) and the recent studies on the effects of mineral oil (Brils *et al.* 2002) and TBT (Meador and Rice 2001; Meador *et al.* 2002) on sediment-dwelling organisms.

Deriving SQGs is controversial because of the many uncertainties in predicting the degree of adverse biological effects caused by sediment-associated contaminants (GIPME 2000). For instance, data on acute toxicity of mineral oil (Brils *et al.* 2002) can be extrapolated to a SQG in different ways. The SL of 200 mg/kg proposed in this paper was derived on the basis of an NOEC for the light oil fractions (C10-19) and the estimated proportion of C10-19 within the total C10-40 fraction. Alternatively, we could have used the LC_{50} for oil of 100 mg/kg (Brils *et al.* 2002). The Dutch procedure for deriving a MTC is to divide the median lethal concentration by 100 (Crommentuijn *et al.* 2000a, 2000b), while in Canada a safety factor of 20 has been suggested by CCME (1995) if the toxicity data are from spiked sediment studies. This yields a SQG for oil of $<5 \text{ mg/kg}$ —a value below all the mineral oil concentrations observed in the harbor sediments and even below the limit of detection. A more appropriate way to identify the actual bioavailability and adverse biological effects to sediment-dwelling organisms of compounds like mineral oil would be to perform separate laboratory bioassays on each of the sediments under investigation.

The chemical data presented in this paper address a suite of contaminants that are of general interest. However, little is known about the presence and toxicity of many thousands of other xenobiotic compounds and their transformation products in the aquatic environment. Analysis of Rhine river water at the port of Rotterdam by means of gas chromatography with mass spectrometric detection (GC-MS) revealed the presence of some 150 'forgotten' compounds such as antioxidants, flame-retardants, and plasticizers (Van der Meulen *et al.* 2001). Hendriks *et al.* (1994) showed that no more than 15% of the toxic effects of Rhine water to the water flea *Daphnia magna* could be attributed to identified compounds, even using sophisticated analytical techniques. Certain compounds with a high octanol–water partition coefficient (e.g. $\log K_{ow} > 3$) might be of relevance in harbor sediments and are currently not included in the our evaluation. It seems virtually impossible to assess all these compounds through chemical analysis and accompanying guideline values. Biological tests or bioassays determine an actual biological response of the mixture of compounds present in contaminated sediments and assess their bioavailability and combined toxicity (Ingersoll *et al.* 1997). For this reason several existing guidelines on the management of dredged material rely on a biological assessment in addition to a chemical screening (US-EPA/US-ACE 1991, 1998; PSSDA 2000; WBTC 2000; Environment Canada 2001; Environment Australia 2002).

Conclusions

A chemical assessment using numeric screening levels for 22 compounds showed that approximately 65% of the volume of dredged material from Dutch harbors has a low probability of causing adverse biological effects. In most sediments, the levels of trace metals, rare earth elements, organochlorine pesticides, and PAHs were not of any environmental concern. TBT, mineral oil, PCBs, and mercury, on the other hand, were identified as important contaminants of concern in Dutch harbor sediments. When it comes to decisions on open water disposal in a high-energy coastal environment, pass/fail criteria for dredged material do not have to be based on normalized concentrations in the harbor sediments. In addition to chemical analysis, risk assessments of the contaminated harbor sediments can benefit from additional measurements on the biological effects by using bioassays.

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